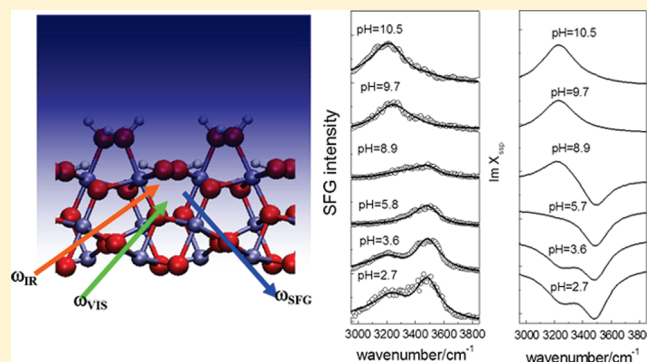


Effect of pH on the Water/ α -Al₂O₃ (1 $\bar{1}$ 02) Interface Structure Studied by Sum-Frequency Vibrational Spectroscopy

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ABSTRACT: Sum frequency vibrational spectroscopy was used to study the structure of water/ α -Al₂O₃ (1 $\bar{1}$ 02) interfaces at different pH values. The OH stretch spectra are dominated by interfacial water contributions at lower frequencies and by bonded hydroxyls on the Al₂O₃ surface at higher frequencies. Protonation and deprotonation of various oxide functional groups at the α -Al₂O₃ surface as pH varies can be monitored quantitatively by changes of the spectrum, allowing extraction of their pK reaction values. The point of zero charge of the interface is found to be at pH \sim 6.7.



INTRODUCTION

Metal oxide surfaces in contact with water are terminated by functional groups that can create local positive or negative charges due to protonation or deprotonation, respectively. Since chemical reactions at oxide/water interfaces, especially those in geochemistry, heterogeneous catalysis, semiconductor processing, electrochemistry, corrosion, and atmospheric chemistry, are very sensitive to both net surface charge and the arrangement of surface charged species,^{1–5} it is crucial to understand protonation/deprotonation processes and the accompanying hydrogen bonding geometry at the molecular level. Much previous work on charging behavior of metal oxide surfaces as pH varies has been done using unspecified powder or polycrystalline materials, which limit systematic evaluation of the results at the molecular level.^{6–9} In contrast, single crystal metal oxides serve as ideal model systems for the fundamental study of water/oxide interfaces, because they allow use of crystallographic controls to select specific surface structure and types of surface functional groups.

We have been systematically studying water/ α -Al₂O₃ interfaces using sum frequency vibrational spectroscopy (SFVS) methodology. α -Al₂O₃ (known as the mineral corundum, with gem varieties sapphire and ruby) is anhydrous and has layers of edge-sharing AlO₆ octahedral units, a structural aspect seen in many minerals, so that it can serve as a proxy surface for studying the interfacial reactivity of clays and various aluminosilicates. Also, artificially grown highly perfect corundum crystals cut to a variety of surface planes are readily obtainable, while many well-ordered natural mineral surfaces and their synthetic analogues are generally difficult to find. Thus, a more complete and less ambiguous interfacial characterization can be done using high-quality synthetic corundum samples.

A fundamental property of the water/oxide interface is the point of zero surface charge (pzc), i.e., the pH value where the surface is electrically neutral. The pzc is determined by the functional groups at the surface and their specific reactivities with respect to protonation/deprotonation. Previous studies on the charging properties of alumina powder have been performed through measurement of electrophoretic mobility or by potentiometric titration. The pzc values for α -Al₂O₃ crystalline powders have been reported to be in the range between pH 8 and 10.^{6–9} In contrast, studies on single-crystal corundum using streaming potential measurements and second harmonic generation (SHG) and SFVS spectroscopy, have produced different results.^{10–17} These studies showed pzc values for α -Al₂O₃ (C, R, and A plane) are all around pH \sim 5 to \sim 6. There have been several suggestions proposed to explain this discrepancy, all of which indicate that the difference in Al–O coordination (and hence types of surface functional groups) is responsible for the large disparity in pzc values.^{10,11,13} It is thus essential to study the molecular details of a particular surface structure if one is to achieve a thorough understanding of the charging behavior and overall reactivity.

SFVS is uniquely suitable for investigating structures of solid/liquid interfaces. It is a second-order nonlinear process that is forbidden in centrosymmetric media but very sensitive to interfacial structure where inversion symmetry is broken. Yeganeh et al. first used SFVS to probe the corundum/water interfacial structure at different pH values, but the crystalline surface they employed was not specified.¹⁴ There have been several recent

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reports of studies on water/ α -Al₂O₃ (0001) interfaces by SFVS.^{15–17} However, to our knowledge, water/ α -Al₂O₃ interfaces cut in different well-defined orientations have not yet been explored by SFVS.

In this paper, we report the SFVS study with phase information on interfacial water structure and charging behavior at the (1 $\bar{1}$ 02) (i.e., R plane) surface of α -Al₂O₃ as a function of pH. We found that each surface vibrational spectrum could be decomposed into two bands, one at \sim 3230 cm⁻¹ and the other at \sim 3490 cm⁻¹. The former varies significantly with pH and can be assigned to interfacial water molecules, while the latter can be assigned to one type of hydroxyl group on the surface. Protonation and deprotonation of the Al₂O₃ surface at different pH values create positive and negative charges on the surface, respectively. The resulting surface fields are expected to induce corresponding net polar orientations of interfacial water molecules, with oxygen and hydrogen terminal atoms facing the interface, respectively. Indeed, we observed a reversal in the sign of the amplitude of the 3230 cm⁻¹ band around pH 6.7, which can thus be identified as the pzc of the water/ α -Al₂O₃(1 $\bar{1}$ 02) interface in agreement with the value deduced in earlier studies.^{18–20} The band at 3490 cm⁻¹ appears to arise mainly from the hydrogen-bonded (H-bonded) hydroxyl groups of AlOH₂ at the surface, as it has a relatively narrow line width, a fixed peak position, and a polarization dependence that closely resembles the band observed on the dry α -Al₂O₃(1 $\bar{1}$ 02) surface.²¹ The sudden decrease of this feature's amplitude with increase of pH from 9 to 10 indicates that the pK value for deprotonation of AlOH₂ is around 9.5. One would anticipate that the α -Al₂O₃(1 $\bar{1}$ 02) surface in water would have the same hydroxyl groups associated with Al₂OH and AlOH₂ as the dry surface.²¹ However, in the SFVS spectrum, the OH stretch mode due to Al₂OH is relatively weak and may be masked by the OH band of the interfacial water. The free OH of AlOH₂ at the dry surface also is observed to disappear, presumably because it is hydrogen bonded to an adsorbed water molecule.

THEORETICAL BACKGROUND

The basic theory of SFVS can be found elsewhere.^{22–25} Here, we present only the essentials needed for the present data analysis. The reflected SF signal is given by

$$S(\omega_{\text{SF}} = \omega_{\text{vis}} + \omega_{\text{ir}}) \propto [\hat{e}(\omega_{\text{SF}}) \cdot \vec{L}(\omega_{\text{SF}})] \cdot \chi^{(2)} : [\hat{e}(\omega_{\text{vis}}) \cdot \vec{L}(\omega_{\text{vis}})] [\hat{e}(\omega_{\text{ir}}) \cdot \vec{L}(\omega_{\text{ir}})] \quad (1)$$

where $\hat{e}(\omega_i)$ and $\vec{L}(\omega_i)$ denote the unit polarization vector and the transmission Fresnel factor at frequency ω_i , respectively. The surface nonlinear susceptibility $\chi^{(2)}$, assumed to be composed of discrete resonances, is described by

$$\vec{\chi}^{(2)} = \vec{\chi}_{\text{NR}}^{(2)} + \sum_q \frac{\vec{A}_q}{(\omega_{\text{IR}} - \omega_q) + i\Gamma_q} \quad (2)$$

where $\vec{\chi}_{\text{NR}}^{(2)}$ is the nonresonant contribution and \vec{A}_q , ω_q , and Γ_q are the amplitude, the resonant frequency, and the damping constant of the q th resonance, respectively. The amplitude A_q in the lab coordinates (i, j, k) is related to the molecular polarizability a_q in the molecular coordinates by

$$A_{q,ijk} = N_q \sum_{\xi, \eta, \zeta} \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta}) \rangle a_{q, \xi \eta \zeta} \quad (3)$$

Using eqs 1 and 2 to fit a measured spectrum allows us to deduce the parameters in eq 2, but the fitting may not be unique unless the resonant frequencies and the sign of $A_{q,ijk}$ are predetermined. The latter often requires a phase measurement of the SFVS signal. To directly characterize the resonances, the $\text{Im } \chi^{(2)}$ spectrum has the expression

$$\text{Im } \vec{\chi}^{(2)} = \sum_q \frac{\vec{A}_q \Gamma_q}{(\omega_{\text{IR}} - \omega_q)^2 + \Gamma_q^2} \quad (4)$$

The sign of A_q describes the absolute orientation of the moiety contributing to the q th resonant mode.

EXPERIMENTAL SECTION

Our SFVS setup has been described elsewhere.^{26,27} In the present case, the input beams, one visible at 532 nm with \sim 500 μJ /pulse and the other tunable infrared between 2.6 and 3.7 μm with \sim 100 μJ /pulse, were incident from the corundum side and overlapped in a spot of $180 \times 300 \mu\text{m}^2$ at the corundum/water interface. The incidence plane was chosen to include the optical axis of the Al₂O₃ crystal so that the polarization of the input beams did not change in passing through the crystal. The two beams had incident angles of $\beta_{\text{vis}} = 45^\circ$ and $\beta_{\text{IR}} = 57^\circ$ at the air/Al₂O₃ interface and the SFVS signal in the reflection direction was spatially and spectrally filtered and collected by a gated detector system. Each data point in a spectrum came from averaging the signals over 200 laser shots and was normalized against that from a z -cut quartz sample. Phase measurement of SFVS was carried out using the interference scheme described previously.^{28–30}

The sample used was an epi-polished single crystal of α -Al₂O₃-(1 $\bar{1}$ 02) purchased from Princeton Scientific Corp. It was 5 mm thick, and the root-mean-square roughness of the polished surfaces was on the order of 0.2 nm. Sample preparation followed the recipe used in earlier work.^{11,13,31} The sample surface was first cleaned in a sonic cleaning bath of acetone, methanol, and pure water for 10, 10, and 60 min, respectively, in sequence. It was then mildly etched in a 10–15 mM solution of HNO₃ under sonic cleaning for 30 min, rinsed thoroughly with deionized water, and blow-dried with filtered dry nitrogen gas. To remove the remaining water and organic contaminants on the surface, the sample was heated at \sim 350 $^\circ\text{C}$ for 1 h in air.²¹

The pH value of deionized water (resistivity 18.3 M Ω ·cm) was controlled by dissolution of sodium hydroxide (99.998% pellets, Sigma-Aldrich) or by addition of hydrochloric acid (37 wt % water solution, 99.999%, Sigma-Aldrich) and was measured by a Beckmann pH meter equipped with an AccuTupH double-junction electrode. Solutions with specific electrolyte concentrations were prepared by dissolving sodium chloride (>99.5%, ReagentPlus, Sigma) into a known volume of water. We did not keep the ionic strength of the solution constant while varying pH because in the pH range we studied; the effect of associated variation of ionic strength on the interfacial properties is small. To confirm this, we measured the changes of the interfacial spectra for solutions of pH 2.5 (\sim 2.5 mM HCl) and pH 11 (\sim 1 mM NaOH) upon dissolution of 50 mM NaCl. Even with such high ionic strength in the solution, the observed changes were much smaller than those observed from varying pH.

RESULTS AND DISCUSSION

The measured SFVS intensity spectra of the α -Al₂O₃-(1 $\bar{1}$ 02)/water interface in the OH stretch region, with SSP

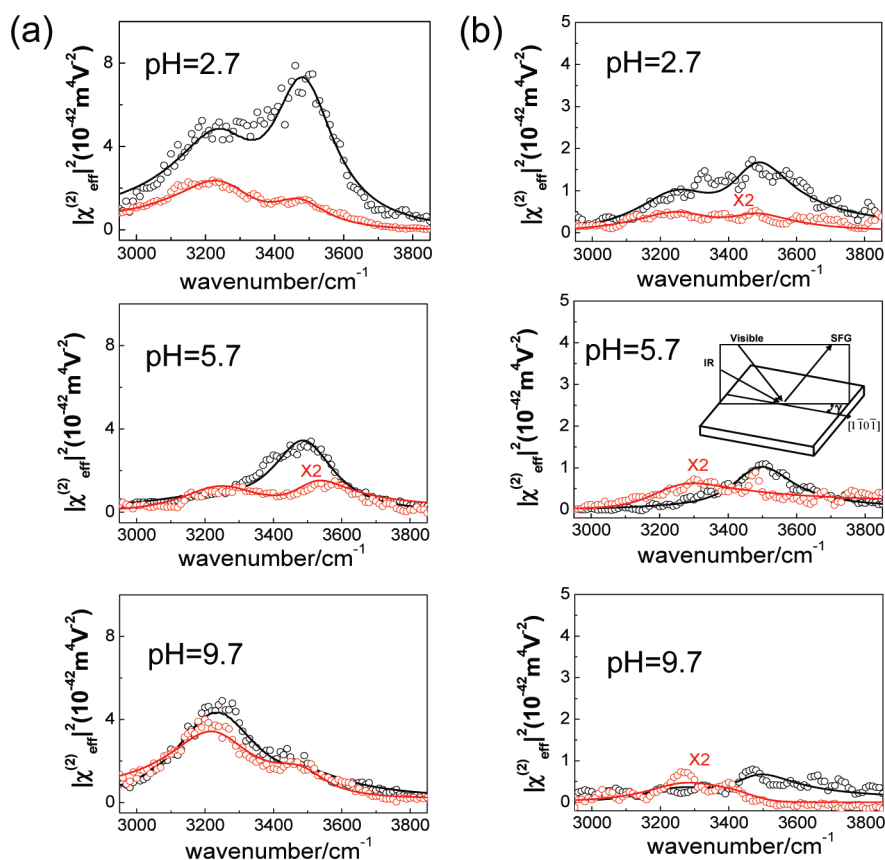


Figure 1. SFVS of $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ /water interfaces with SSP and SPS polarization combinations at three different pH values: 2.7 (top), 5.7 (middle), and 9.7 (bottom), where red and black circles describe the spectra at $\gamma = 0^\circ$ and 180° , respectively. ($\times 2$ indicates amplifying the spectra by 2 times in order to clearly show the spectral features.)

(denoting s-, s-, p-polarized SFVS output and visible and infrared inputs, respectively) and SPS input/output polarization combinations, are presented in Figure 1 for three different values of pH in water. Red and black curves in the spectra describe sample positions of $\gamma = 0$ and $\gamma = 180^\circ$, respectively, where γ is defined as the angle of the $[1\bar{1}0\bar{1}]$ direction with respect to the incident plane, illustrated in the inset of Figure 1. All spectra can be fitted using eqs 1 and 2 with two resonant bands with frequencies (ω_q) of 3230 and 3490 cm^{-1} and linewidths (Γ_q) of 150 and 110 cm^{-1} , respectively. The strength (A_q) of each band changes with pH and γ , and their signs were determined by separate SFVS phase measurements. We plot in Figure 2 the corresponding $\text{Im}\chi^{(2)}$ spectra calculated from eq 4 using the parameters, ω_q , Γ_q , and A_q , deduced from the fitting. They show more clearly the two resonant bands with appropriate signs. In Figure 3 a more complete set of $|\chi^{(2)}|^2$ and $\text{Im}\chi^{(2)}$ SSP spectra with different pH is given, and the amplitudes for the two bands deduced from fitting are plotted in Figure 4. We see in Figure 4a that the amplitude of the 3230 cm^{-1} band responds to pH in two steps. It changes smoothly from a significant negative value to nearly zero when pH increases from 3.5 to 5.5 and from zero to a significant positive value when pH increases from 8 to 10. The amplitude of the 3490 cm^{-1} band appears to have only a single step of significant change occurring between pH 9 and 10. Such step changes of the amplitudes should be related to the protonation/deprotonation reactions at the water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interface.

The observed spectra must come from OH stretches of the interfacial water molecules and/or OH species residing on the $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface. To understand the spectra, we need to know first what OH species could exist on the $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface. In our earlier work, we found that the dry $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface has a structure composed of three relaxed layers in which oxygen atoms are bonded to one, two, and three Al molecules, respectively, as shown in Figure 5.^{21,32} This surface has C_{1v} symmetry with respect to the $(\bar{1}\bar{1}20)$ glide plane. Protonation of the surface leads to the appearance of three OH species, two bonded OH (H bonded to a neighboring acceptor O) associated with Al_2OH and AlOH_2 and one free OH associated with the AlOH_2 functional group. These hydroxyls have their stretch mode frequencies at ~ 3365 , 3520, and 3670 cm^{-1} , respectively, and corresponding orientations of $\theta \sim 69^\circ$ and $\varphi \sim \pm 67^\circ$, $\theta \sim 62^\circ$ and $\varphi \sim \pm 127^\circ$, and $\theta \sim 36^\circ$ and $\varphi \sim \pm 78^\circ$, respectively. Here, θ is the polar angle of OH away from the surface normal and φ is the azimuthal angle of OH away from the $[1\bar{1}0\bar{1}]$ direction in the surface plane. The strengths of the different bands in the SFVS vibrational spectrum depend on the orientations of the OH species. As a result, the 3520 and 3670 cm^{-1} bands in the SSP spectrum are relatively strong and the 3365 cm^{-1} band weak. Because of its high bond valence value, oxygen in the Al_3O functional group at the $(1\bar{1}02)$ surface is not easily protonated in air. At the water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interface, we expect that the three oxide groups, Al_3O , Al_2O , and AlO groups can be protonated or deprotonated, depending on the contacting solution pH. References 18–20 provide estimated pK values for protonation/

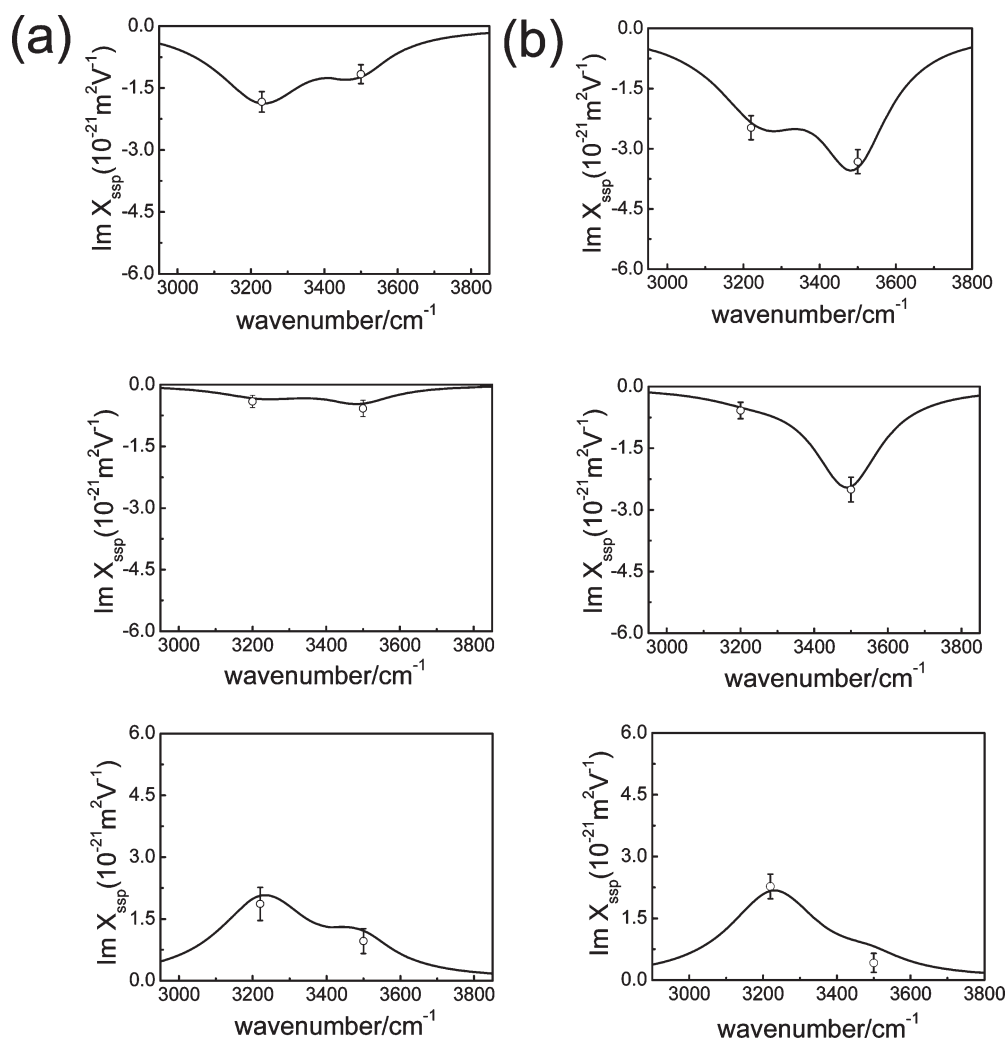
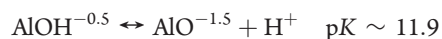
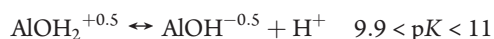
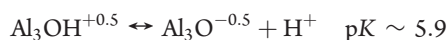


Figure 2. $\text{Im } \chi_{\text{ssp}}^{(2)}$ spectra deduced from the corresponding $\text{SSP-}|\chi^{(2)}|^2$ spectra in Figure 1: (a) $\gamma = 0^\circ$ and (b) $\gamma = 180^\circ$ with pH 2.7 (top), 5.7 (middle), and 9.7 (bottom). The circles are data points obtained directly from SFVS phase measurements.

deprotonation reactions of the different relevant groups



where the superscript on a molecular group denotes the formal charge on the group assuming typical Pauling bond valence criteria.¹⁹ Using eq 5 as guidance, we expect the following surface structures: For pH decreasing from 6, the surface gets increasingly positively charged through protonation of the Al_3O groups until saturation occurs; so the surface is mainly composed of Al_2OH and AlOH_2 groups and Al_3O and Al_3OH groups balanced by the protonation/deprotonation reaction. For pH increasing from 6, the surface becomes increasingly negatively charged through deprotonation of the AlOH_2 groups and is mainly composed of Al_3O and Al_2OH groups and AlOH_2 and AlOH groups balanced by

their protonation/deprotonation reaction. Around pH 6, the surface is essentially neutral and composed of Al_3O , Al_2OH , and AlOH_2 groups. In all cases, interfacial water molecules can be H bonded to the surface: they have their hydrogen H bonded to the oxygen of the deprotonated sites and their oxygen bonded to the hydrogen of the otherwise free OH on the AlOH_2 groups.

We now discuss how we can understand the OH stretch bands in the spectrum of the water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interface and their variation with pH. Considering first the 3230 cm^{-1} band, which resembles the so-called “icelike” band often seen in the SSP SFVS spectrum of other water interfaces, we believe it comes mainly from interfacial water molecules. As seen in Figure 4, the amplitude of this band changes from negative to positive sign when the pH of interfacial water changes from a low to a high value, while in the middle pH range, it is very weak. This is characteristic of a SFVS spectrum for interfacial water near a surface that can be protonated and deprotonated.^{14,15} The negative and positive band amplitudes correspond to net polar orientations of interfacial water molecules with their oxygen and hydrogen ends, respectively, facing the crystalline surface. Protonation and deprotonation of the oxide surface can reorient the interfacial water molecules through the surface charges (and hence, the surface field) they created and through change of the

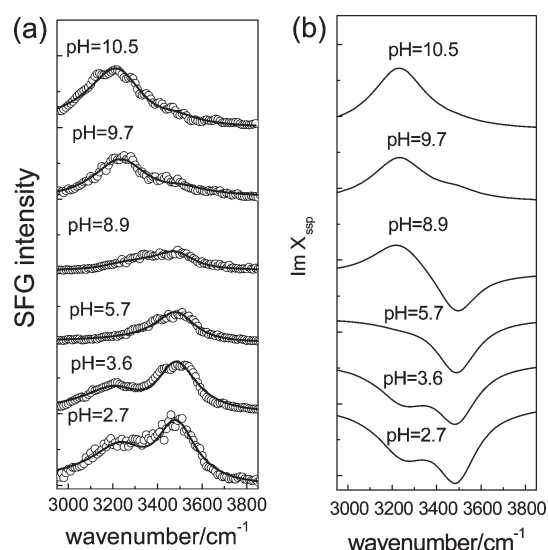


Figure 3. SSP spectra of (a) $|\chi_{\text{SSP}}^{(2)}|^2$ and (b) $\text{Im } \chi_{\text{SSP}}^{(2)}$ for $\alpha\text{-Al}_2\text{O}_3(1102)$ /water interfaces at several different pH values at $\gamma = 180^\circ$.

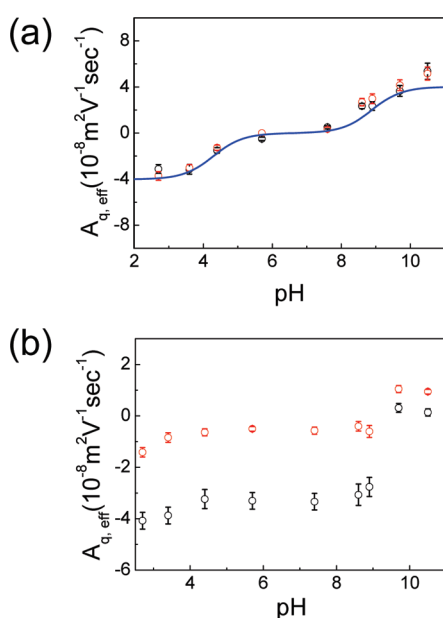


Figure 4. Amplitudes of the OH stretch modes at (a) 3230 cm^{-1} and (b) 3490 cm^{-1} vs pH. The blue curve in (a) is a theoretical fit (described in the text). Red and Black circles in (b) describe data points for $\gamma = 0$ and 180° , respectively.

bonding geometry of the water molecules at the surface. Both mechanisms appear to reorient interfacial water molecules in the same average direction. Negatively charged deprotonated oxide sites tend to reorient interfacial water molecules with H pointing toward the interface by the negative surface field they create and by the H-bonds they tend to establish with H of the water molecules. The protonated sites function the opposite way. In the case of the $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface, protonation of the Al_3O groups and deprotonation of the AlOH_2 groups lead to positive and negative surface charges, respectively. Thus, variation of the 3230 cm^{-1} band with pH depicted in Figures 3 and 4 shows that the alumina surface is negatively charged at high pH and positively charged at

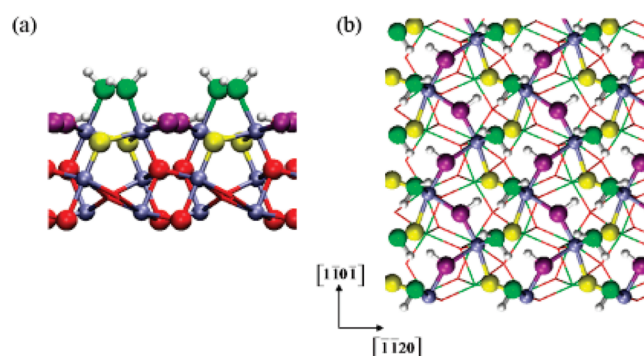


Figure 5. Protonated surface structure of $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ deduced from SFVS spectra and CTR measurements: (a) side view and (b) top view.

low pH. In the middle pH range, the band amplitude is very low, which is characteristic of a neutral water interface with little net dipolar orientation of the water molecules. This is clear evidence that this band is mostly from interfacial water molecules. If it were from OH species associated with the $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface, then its resonance amplitude could never change sign despite changes in its absolute strength due to protonation or deprotonation. We can calculate the surface concentrations of Al_3OH and AlOH , which carry a charge of $+1e$ and $-1e$, respectively, and hence, the surface charge density versus pH from the protonation reaction, $\text{Al}_3\text{OH} \leftrightarrow \text{Al}_3\text{O} + \text{H}$, and the deprotonation reaction, $\text{AlOH}_2 \leftrightarrow \text{AlOH} + \text{H}$, if we know their respective pK values. In Figure 4a, by assuming that the band amplitude is proportional to the surface charge density and using the two pK values as adjustable parameters, we can actually fit the data fairly well. We find from the fit, $\text{pK} = 4.9 \pm 0.4$ and 9.2 ± 0.5 for the protonation and deprotonation reactions mentioned above. They are reasonable when compared with the corresponding estimated pK values given in eq 5. We note also from the previous SFVS result on the dry $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface, that the Al_2OH groups on the surface may contribute to a resonance band around 3365 cm^{-1} . However, this band is rather weak and is negligible compared to the 3230 cm^{-1} water band. The other OH species from Al_3OH , AlOH_2 , and AlOH groups also do not seem to contribute significantly to this water band due to H-bonding with water molecules.

We next consider the 3490 cm^{-1} band in the SFVS spectrum of the water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interface. As seen in Figure 4b, the amplitude of this band is negative at all pH except for $\gamma = 0$ and $\text{pH} > 9$, suggesting that it largely originates from $\text{O} \rightarrow \text{H}$ pointing away from the interface. Its frequency is close to the 3520 cm^{-1} band observed on the dry surface, and therefore we can similarly identify it as mainly coming from the OH species of AlOH_2 that is H-bonded to neighboring O in the surface lattice. This assignment is supported by several observations. Compared to the band observed from the dry surface, it has the same strong forward ($\gamma = 0^\circ$)–backward ($\gamma = 180^\circ$) asymmetry in strength, and is red-shifted by 30 cm^{-1} . Its somewhat broader line width is likely due to interaction with surrounding water. We can extract the orientation of OH from the 3490 cm^{-1} band in the SSP and SPS spectra of Figure 1 using the same procedure outlined in refs 21, 33, and 34. We find, independent of pH, an orientation specified by $\theta = 58^\circ \pm 15^\circ$ and $\varphi = \pm 118^\circ \pm 13^\circ$, which is very close to the orientation, $\theta = 62^\circ \pm 8^\circ$, $\varphi = \pm 127^\circ \pm 9^\circ$, of the same OH species on the dry surface.²¹ Finally, we notice in Figure 4b that the band amplitude A_q changes abruptly at $\text{pH} \sim 9$,

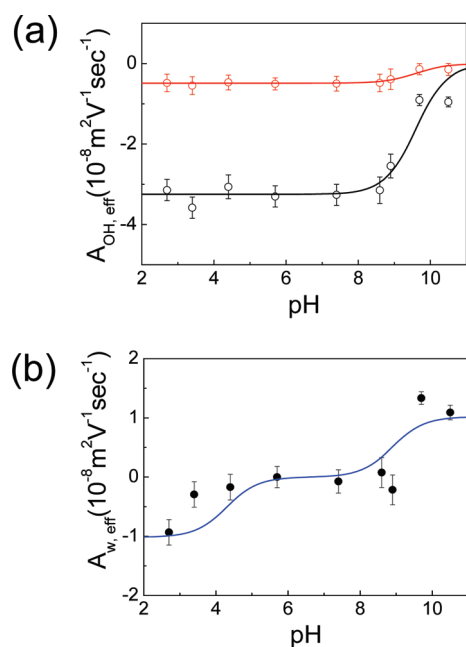


Figure 6. Contributions to the 3230 cm^{-1} band from (a) OH on AlOH_2 and (b) water vs pH. Red and black circles in (a) refer to data points of $A_{\text{OH}}(\gamma = 0^\circ)$ and $A_{\text{OH}}(\gamma = 180^\circ)$, respectively, for OH on AlOH_2 and the lines are a theoretical fit (described in the text).

which is close to the pK value of the protonation/deprotonation reaction $\text{AlOH}_2 \leftrightarrow \text{AlOH} + \text{H}$. Thus we believe we can confidently assign the 3490 cm^{-1} band to the H bonded OH stretch on AlOH_2 . However, interfacial water molecules generally also contribute a “liquid-like” band to this spectral range that may not be negligible. In our case, this is evidenced by the observed positive amplitude at $\text{pH} > 9$ with $\gamma = 0$ in Figure 4b since OH on AlOH_2 pointing away from the surface can only contribute negatively to A_q . We can separate the contributions from water and AlOH_2 to the OH band (still approximating it as a single mode), knowing that OH of AlOH_2 has strong forward–backward anisotropy (Figure 1) which the interfacial water molecules cannot exhibit. The observed SF amplitudes, $A_q(\gamma = 0^\circ)$ and $A_q(\gamma = 180^\circ)$, in the forward and backward directions consist of components A_w from water and $A_{\text{OH}}(\gamma = 0^\circ)$ and $A_{\text{OH}}(\gamma = 180^\circ)$ from OH on AlOH_2

$$A_q(\gamma = 0^\circ) = A_{\text{OH}}(\gamma = 0^\circ) + A_w \text{ and}$$

$$A_q(\gamma = 180^\circ) = A_{\text{OH}}(\gamma = 180^\circ) + A_w \quad (6)$$

$A_{\text{OH}}(\gamma = 0^\circ)$ and $A_{\text{OH}}(\gamma = 180^\circ)$ are proportionally related because they come from the same OH species: $A_{\text{OH}}(\gamma = 0^\circ) = \kappa A_{\text{OH}}(\gamma = 180^\circ)$. The proportional constant κ can be obtained from the measured $A_q(\gamma = 0^\circ)$ and $A_q(\gamma = 180^\circ)$ at $\text{pH} \sim 6$ where the water contribution A_w is known to be negligible. We can thus separately deduce A_w , $A_{\text{OH}}(\gamma = 0^\circ)$, and $A_{\text{OH}}(\gamma = 180^\circ)$. The results plotted as functions of pH are presented in Figure 6. It is seen in Figure 6a that $A_{\text{OH}}(\gamma = 0^\circ)$ and $A_{\text{OH}}(\gamma = 180^\circ)$ are always negative and remain nearly constant until $\text{pH} \sim 8.5$, and then drop off to a small value at $\text{pH} \sim 10$. Knowing that A_{OH} is proportional to the surface density of AlOH_2 , we can calculate A_{OH} from the deprotonation reaction $\text{AlOH}_2 \leftrightarrow \text{AlOH} + \text{H}$. The solid curves in Figure 6a calculated with $pK = 9.2$ for the reaction fit the data quite well. The water contribution A_w at different

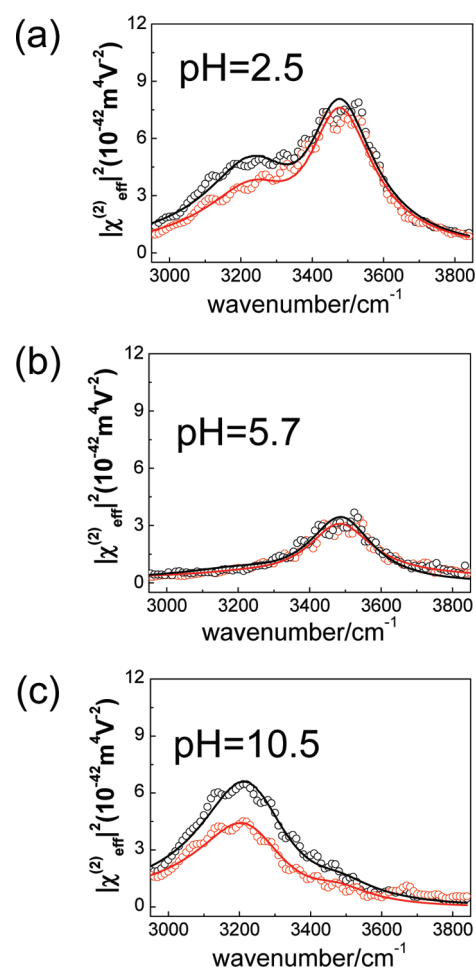


Figure 7. SSP spectra of $\alpha\text{-Al}_2\text{O}_3$ ($1\bar{1}02$)/water interfaces at $\gamma = 180^\circ$ for three different pH values, 2.4 (top), 5.7 (middle), and 10.5 (bottom) with (red circles) and without (black circles) addition of 50 mM of NaCl in the water solution.

pH is plotted in Figure 6b. The data, although of poorer quality, show a similar two-step change with pH as that of the 3230 cm^{-1} band of water in Figure 4a. They can also be roughly fitted by the protonation reaction $\text{Al}_3\text{OH} \leftrightarrow \text{Al}_3\text{O} + \text{H}$ with $\text{pH} 4.9$ and the deprotonation reaction $\text{AlOH}_2 \leftrightarrow \text{AlOH} + \text{H}$, with $pK = 9.2$, assuming that A_w is proportional to the surface charge density. Negative and positive A_w at low and high pH values reflect the presence of positive and negative charges at the surface.

There are other hydroxyl groups attached to the $\alpha\text{-Al}_2\text{O}_3$ -($1\bar{1}02$) surface that could contribute to the OH stretch spectrum in the pH ranges we have studied but cannot be identified in our spectra. These are OH species associated with Al_2OH that exist at all pH, with AlOH at $\text{pH} > \sim 9$, with AlOH_2 at $\text{pH} < \sim 9$ (referring to the originally dangling OH on the dry surface), and with Al_3OH at $\text{pH} < \sim 5$. As we mentioned earlier, the band associated with Al_2OH is relatively weak and likely negligible. The originally dangling OH on AlOH and AlOH_2 is suppressed by H-bonding to a water molecule if the surface is submerged in water. Because its H-bonding strength with water can vary over a wide range, this OH band may have a low peak strength and very broad bandwidth, causing it to be indistinguishable from other bonded OH bands. Finally, the OH species on Al_3OH is expected to be weak because O is already strongly bonded to three Al molecules, and its stretch

frequency may appear below the spectral range we have studied. Thus the OH species of AlOH_2 that is H-bonded in the surface lattice appears to be the only one contributing significantly and distinctively in the SFVS spectrum.

We can determine the point of zero charge (pzc) of the water/R-sapphire interface from the curve of the 3230 cm^{-1} band amplitude versus pH in Figure 4a, assuming that the amplitude is proportional to the surface charge density as we discussed earlier. The nearly zero amplitude at $\sim 5.7 < \text{pH} < \sim 7.8$ indicates that the interface is neutral in that range. The pzc is found to be at $\text{pH} \sim 6.7$, which is close to the theoretically predicted pzc of $\text{pH} \sim 7.8^{18-20}$ and the experimentally measured pzc of 5.2 by second harmonic generation.¹⁵ To be sure that the nearly zero strength of the water band represents a neutral interface, we have measured the spectral changes upon addition of salt to the water solutions at different pH values. The interfacial water spectrum is expected to change if salt ions are attracted to the charged surface but not if the surface is neutral. We present in Figure 7 the SFVS spectra of water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interfaces with and without 50 mM NaCl in water at $\text{pH} = 2.4, 5.7,$ and 10.5 . It is seen that with NaCl, the water band is clearly reduced for pH at 2.4 and 10.5 (because of screening of the surface field by ions) but is weak and hardly changed at $\text{pH} 5.7$ as expected from a neutral interface. We also notice that in all cases, the $\sim 3490\text{ cm}^{-1}$ band is not much affected by the addition of salt, providing additional evidence that this band is dominated by hydroxyls on the $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ surface, with little contribution from interfacial water molecules.

CONCLUSION

We have used SFVS to study the structure of water/ $\alpha\text{-Al}_2\text{O}_3(1\bar{1}02)$ interfaces as a function of pH. The spectra in the OH stretch region exhibit two bands at ~ 3230 and $\sim 3490\text{ cm}^{-1}$ that can be identified as coming mainly from interfacial water molecules and the H-bonded hydroxyl associated with the AlOH_2 groups on the surface of $\alpha\text{-Al}_2\text{O}_3$, respectively. Protonation and deprotonation of the oxide sites at the surface can be monitored by the spectral change of the SFVS water band because the field created by the surface charges can reorient the interfacial water molecules. Using these assumptions, we deduce pK values of 4.9 and 9.2 for the protonation/deprotonation reactions of Al_3OH and AlOH_2 groups at the surface, respectively. The same pK value of 9.2 is also obtained from the spectral change of the 3490 cm^{-1} band for OH on AlOH_2 . Variation of the water band with pH also allows us to find the range of pH in which the interface is neutral, and thus determine that the point of zero charge of the interface is at $\text{pH} \sim 6.7$. This work provides another example that surface-sensitive SFVS is an effective tool for probing structures of relevant oxide/water interfaces at the molecular level and shows that different crystalline surfaces of the same crystal may behave differently in relation to their different surface structures. To further explore the last point, we are in the process of studying the A-plane ($11\bar{2}0$) Al_2O_3 surface using SFVS.

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